

II.E.2 Membrane/Electrolyzer Development in the Cu-Cl Thermochemical Cycle

M.A. Lewis (Primary Contact), S. Ahmed,
Serguei Lvov¹, Chinbay Fan²

Argonne National Laboratory

9700 S. Cass Avenue

Argonne, IL 60439

Phone: (630) 881-5973

Email: lewism@cmt.anl.gov

¹Pennsylvania State University, University Park, PA

²Gas Technology Institute (GTI), Des Plaines, IL

DOE Manager

HQ: Sara Dillich

Phone: (202) 586-7925

Email: Sara.Dillich@ee.doe.gov

Start Date: October 2010

Projected End Date: September 2012

FY 2012 Accomplishments

- Showed that both a Nafion[®]-based membrane and a porous polyethylene (PPE) membrane inhibited copper transport from the anode to the cathode.
- Demonstrated that the hydrogen production efficiency exceeded >95% when the cell potential was stable at 0.7 V and the current density was 0.5 A/cm² using a Nafion[®]-based membrane and observed no copper deposits on any of the cell components after a 36 h test.
- Fabricated a full-scale, single-cell electrolyzer which had a current density of 0.18 A/cm² for a cell voltage of 0.7 V.
- Continued collaborations with Atomic Energy of Canada Limited and a group of Canadian universities.



Fiscal Year (FY) 2012 Objectives

- Identify methods that prevent copper deposition at the cathode of the electrolyzer while meeting targets for cell potential (0.7 V) and current density 0.3 A/cm² in 2012.
- Start development of a full size electrolyzer, 300 cm².
- Continue collaborative work on the thermal reactions with Canada.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(U) High-temperature Thermochemical Technology

(V) High-Temperature Robust Materials

(W) Concentrated Solar Energy Capital Cost

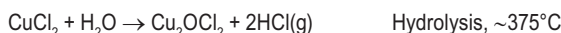
Technical Targets

The technical targets are the cost of hydrogen production and the process energy efficiency.

- For 2017, these are \$2.00 per gasoline gallon equivalent (gge) H₂ and >35% (lower heating value), respectively.

Introduction

The U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy is supporting the development of hydrogen production technologies that use solar heat. One approach involves thermochemical cycles whose heat source is the solar power tower, which is near commercialization and provides heat near 550°C now and at higher temperatures in the future. The CuCl cycle is unique because its maximum temperature is less than 550°C. The three major reactions in the Cu-Cl cycle are shown below.



All reactions have been verified at the temperatures shown. Note that the maximum temperature is less than 550°C. No separations or phase changes are specified in this high level representation.

Because there is a potential for catastrophic failure of the electrolysis cell if copper crossover and deposition occur and because the electrical energy consumed during electrolysis is a major component of the energy usage, our focus has been on optimizing the electrolyzer's performance, i.e., maximizing current density for a given voltage while eliminating parasitic reactions. Copper crossover must be minimal. Cell voltage needs to be as low as possible to reduce energy usage and the current density has to be as high as possible to minimize capital costs and maximize hydrogen production efficiency.

Approach

The approach for improving electrolyzer performance was threefold: (1) further improve membrane properties to reduce copper crossover, (2) modify the electrolyzer's hardware and operating parameters to increase current density for cell potentials of 0.7 V and less, and (3) develop a methodology to study long-term durability of the electrolyzer and determine degradation mechanisms. To improve the very thin (1-mm thick) porous polyethylene membrane's mechanical stability, various coatings were applied and tested. The Nafion[®]-based membrane is a hot pressed material and differences in pressing procedures were investigated. Different procedures and configurations were investigated for fabricating membrane electrode assemblies. Various changes in hardware and operating parameters, such as flow rates, catalysts and catalyst loadings, as well as anolyte and catholyte compositions are being investigated to determine their effect on cell performance and their potential to reduce costs and/or increase efficiency. For example, we identified changes in flow field designs as having an impact on performance with the porous polyethylene membrane. Some tests with the Nafion[®]-based membrane gave very stable cell potentials while a few did not. Electrochemical impedance spectroscopy will be used to determine degradation mechanisms with the goal of improving lifetime performance. A 6.45 cm² single cell was used for this work.

In addition, a full-size, 300-cm² active area, single cell was fabricated. It is expected that different challenges, e.g., sealing and minimization of shunt current, will need to be addressed but that the work on membranes, degradation mechanisms, etc., will extend to larger scale work.

Results

Characterization of Membranes (S.Lvov, PI)

Potential membrane materials were screened using permeability of dissolved Cu(II) species and conductivity at 25°C. The methods and equipment were carefully verified. Details of the equipment and methods will be published elsewhere. Table 1 contains a comparison of these properties, selectivity values (defined as the ratio of conductivity to permeability, or the ratio of hydrogen transport to copper transport), as well as current costs for Nafion[®] 117, Nafion[®]-

TABLE 1. Properties of Membranes for Possible Use in the Cu-Cl Electrolyzer

Property	Conductivity (S/cm)	Permeability x 10 ⁻⁸ (cm ² /s)	Selectivity x 10 ⁶ (S·s/cm ²)	Today's Cost (\$/m ²)
Nafion [®] 117	0.083	1.8	4.61	550
Nafion [®] -based	0.057-0.076	0.15-1.92	<39.5	>550
PPE	0.050	1.6	3.1	10*

*Does not include coating costs

based and PPE. Cost is also a factor in the evaluation of the various membranes. As can be seen, the cost of the porous polyethylene is about 55 times less than that of Nafion[®]117. However, the cost for the Nafion[®]-based membranes will be greater than that of Nafion[®]117 because of additional processing. While PPE is the least expensive, it may require a coating for additional mechanical stability and that cost is unknown. Several coatings have been tried but none has proven completely satisfactory.

Electrolyzer Performance with Nafion[®]-Based Membranes (S.Lvov, PI)

A schematic of the electrolyzer is shown in Figure 1. The ancillary equipment was redesigned to allow for recycling the solutions and to maintain a safe working environment and reliable operation. Fabrication was completed in late 2011. Teflon[®] or perfluoroalkoxy components replaced all metallic components. Teflon[®] diaphragm pumps replaced unreliable peristaltic pumps. The HCl concentration in the anolyte and catholyte was reduced from 11M to 6 or 7M. The CuCl concentration was 2M. Additional heating tapes, insulation and oil baths for bringing the recycled solutions to test temperature were incorporated into the design. H₂ production was measured by weighing the water displaced by the exit gas after drying and HCl removal. Additional information on the apparatus and test protocol will be published elsewhere.

Figure 2 shows a polarization curve using the Nafion[®]-based membrane for two flow rates after a 24-h test. The tests were run at 80°C, atmospheric pressure, and 0.8 mg/cm² Pt loading on the Nafion[®]-based membrane. The flow field was serpentine. At the target voltage of 0.7 V, the measured current densities were 0.46 and 0.51 A/cm² for flow rates of 59 and 130 mL/min, respectively. These values exceed our 2012 milestone value and approach our 2015 target. Figure 3 shows that the hydrogen production efficiency was 95-100% for the 24 hour period, i.e., the experimental values were within a few percent of the values predicted by Faraday's Law. Such hydrogen production efficiency indicates there were no parasitic losses due to reduction of copper ions. No copper deposits were visually observed on any of the components of the cell after the tests. A subsequent test was run for 36 h with the same results. However, one test showed decreasing current density with time. The mechanism for the degradation of performance is not understood at this time and electrochemical impedance spectroscopy will be employed in future tests.

Electrolyzer Performance with PPE Membrane (C. Fan, PI)

Tests were conducted at 0.7 V with this membrane in a small electrolyzer, active area of 6.45 cm², at 80°C with deionized water as the catholyte and 2 mol CuCl in 10 mol/L HCl as the anolyte. Of the two flow fields studied,

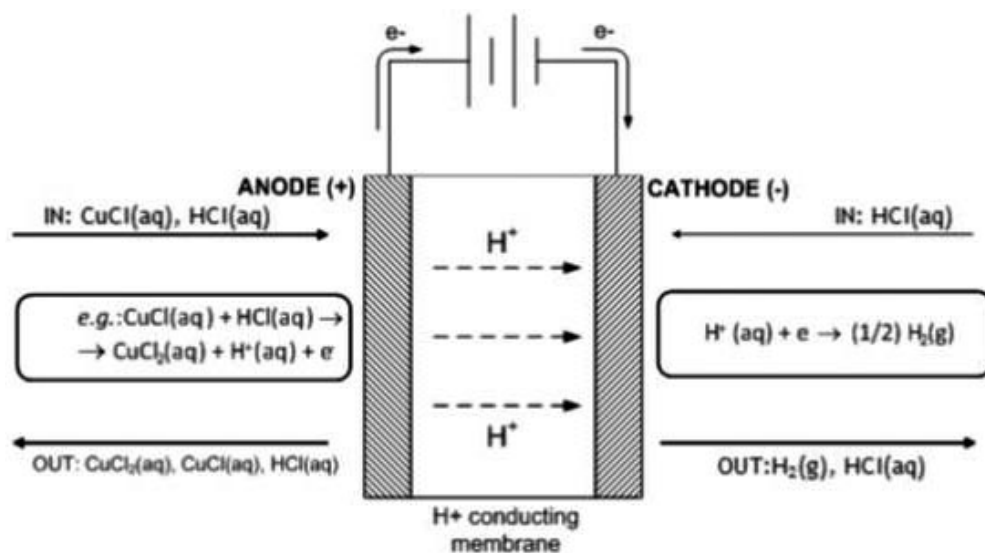


FIGURE 1. Schematic of the electrolysis cell for the CuCl cycle

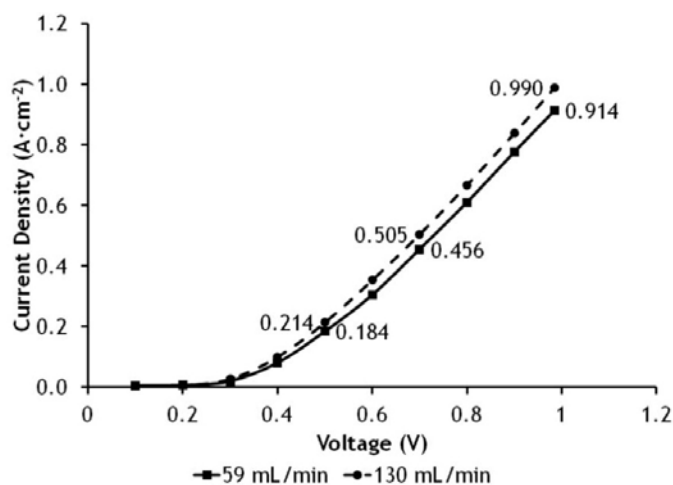


FIGURE 2. Polarization curve for the CuCl electrolysis with Nafion®-based membranes at two flow rates after 24 h

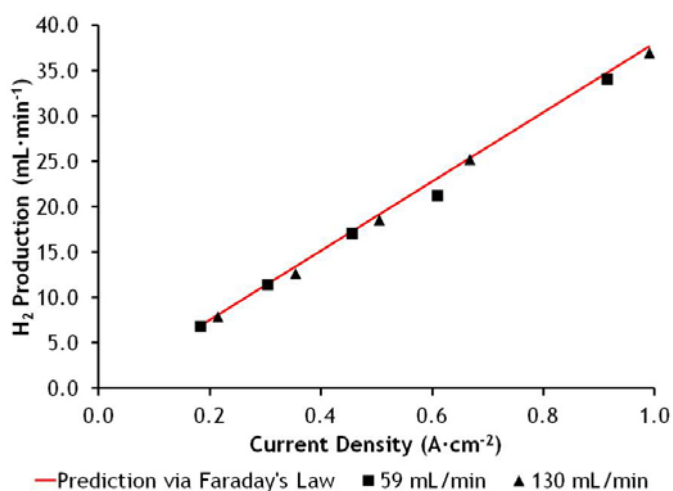


FIGURE 3. Hydrogen production efficiency versus time for the experiment described in Figure 2

the serpentine flow field had a slightly lower current density (0.12 A/cm^2) than the carbon felt design (0.16 A/cm^2) when the Pt loading was 0.5 mg/cm^2 on both the anode and cathode. The type of coating on the membrane had a significant effect. For example, for the same Pt loading on the carbon felt cathode (0.5 mg/cm^2 but none on the anode), the current density was 0.3 A/cm^2 when the PPE membrane was coated with a ceramic and 0.19 A/cm^2 when coated with Nafion®. When PPE was coated with Nafion® and the Pt loading was decreased from 2.0 to 0.5 mg/cm^2 , the current density was only marginally impacted as it decreased from 0.19 to 0.18 A/cm^2 . These results suggest that a carbon felt flow field, a ceramic coating on PPE, and 0.5 mg Pt/cm^2

are preferred to a serpentine flow field and no coating or a Nafion® coating on the PPE membrane.

GTI's primary focus is the development of a 300 cm^2 -size electrolyzer, dimensions 14.6 cm by 20.8 cm . Figure 4 shows GTI's polarization curve for a single cell. The current density was 0.18 A/cm^2 at 0.7 V . Conditions for this test were 62°C , 1 bar , PPE membrane with Nafion® coating, 0.5 mg/cm^2 Pt on cathode and anode, carbon felt on both anode and cathode, water as catholyte and 1 mol CuCl in a 10 mol/L HCl as anolyte, 1 L/min flow rate. Changes in operating conditions are being investigated to increase current densities in these full-scale electrolyzers. In addition, work is in progress to develop a multi-cell stack. Issues that

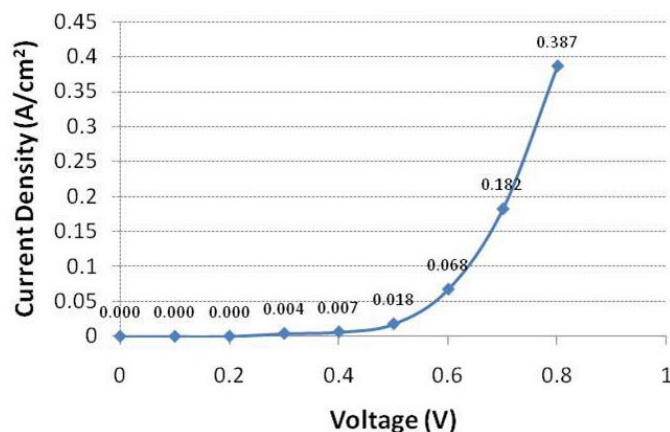


FIGURE 4. Polarization curve for a single cell electrolysis cell with 300 cm² of active area

are being addressed include sealing of the cell, distributing mass of the anolyte/catholyte evenly through all cells in the stack, maintaining good electric contact within each cell and minimizing shunt current.

Collaborations

Atomic Energy of Canada Limited and five Canadian universities are working on the development of the CuCl cycle. The collaboration consists of an informal information exchange. Significant progress has been made recently. For example, Atomic Energy Canada Limited invented a new electrolyzer design that inhibited essentially all diffusion of dissolved copper species to the catholyte for up to 341 h. The measured dissolved copper concentration remained stable at 1-2 ppm during the entire run time.

An integrated demonstration is planned for 2013-2014 at the University of Ontario Institute of Technology. A building is dedicated for this purpose. The equipment for the hydrolysis and oxychloride decomposition reactions and other processes, such as crystallization, are now undergoing hot tests prior to their integration. Direct contact cooling of the molten CuCl in water has been tested. Steam was generated from the direct quench. The molten CuCl droplets solidified and subsequently disintegrated into small pieces within two seconds. No steam explosion was observed.

Conclusions

- Achieved current densities that exceed our 2012 milestone when the cell voltage was 0.7 V using the Nafion®-based membrane.
- Conducted electrolyzer tests that showed no visible copper deposition in/on the cell components.
- Successfully tested a single cell electrolyzer with an active area of 300 cm² and started fabrication of a full scale multi-cell stack.

Future Directions

- Extend duration of the electrolyzer tests with the Nafion®-based membrane.
- Develop methods to improve the mechanical stability of the PPE membrane.
- Continue improvement of the electrolyzer's performance by investigating other compositions for the anolyte and catholyte, flow rates, flow field design, electrode surface, mass transport media, etc. to obtain higher current densities at 0.7 V.
- Fabricate and test a multi-cell stack full size electrolyzer and improve its performance to meet the current density milestone.
- Investigate the degradation mechanisms in the electrolyzer and develop methods to mitigate these.
- Continue collaboration with staff at Atomic Energy of Canada Limited and six Canadian universities; sharing experimental data and approaches to leverage R&D funds.

FY 2012 Publications/Presentations

1. CuCl Electrolysis for Hydrogen Production in the Cu-Cl Thermochemical Cycle, R. Sharna, M. Fedkin, and S. Lvov, *J. Electrochem. Soc.*, 158(3) B266-B275 (2011).
2. G.F. Naterer et al., Clean Hydrogen Production with the Cu-Cl Cycle - Progress of International Consortium, I: Experimental Unit Operations, *Int. J. Hydrogen Energy*, 36, 15472-15485 (2011).
3. M.A. Lewis et al., Recent Advances in the U.S. R&D Program for the Cu-Cl Cycle, Ontario Research Foundation Workshop, Chalk River, Canada, Nov. 9, 2011.
4. M.A. Lewis et al., Electrolyzer Development for the Cu-Cl Thermochemical Cycle, Ontario Research Foundation Workshop, Oshawa, Ontario, Canada, May 10, 2012.